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The preparation of zinc chloride from smelter waste

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THE PREPARATION OF ZINC CHLORIDE FROM SMELTER WASTE.

BY

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INTRODUCTION.

Interest in the matter of recovering zinc from residual material attaches through the value of a practical method of recovery consistent with commercial operations. The material used in this work at the Missouri School of Mines and Metallurgy was supplied by one of the large chemical firms of Saint Louis. It was impossible to obtain more than the merest suggestion intimating that the solution of the problem was of considerable importance to the company. Their business secrets permitted of no detailed disclosures but there was reason to believe that quite a material profit lay in finding a means of more satisfactory manufacture than they were employing in the production of zinc chloride. Their interest in this matter induced them to ship about three hundred pounds of "residue" to us as a basis for experimentation and research.

In this work thanks must be acknowledged for the many and helpful suggestions of Dr. W.D.Turner, and for the timely assistance of Professor C.Y.Clayton, and for the invaluable supervision of Professor K.K.Kershner.

GENERAL CONSIDERATIONS.

No particulars concerning the origin or previous treatment of the product submitted for investigation were offered by way of indicating the procedures to be tried here. The problem was as complete an extraction of zinc as possible from the material which was sent here. It was suggested, however, that jigging might furnish a satisfactory means of concentrating the zinc-bearing portions.

The material was found to be dark gray in color and had the appearance of cinders except for being denser and free from sharp edges. The lumps varied in size from irregular pieces, three to four inches long and almost as thick, down to particles having a diameter of one half inch. The larger particles readily crumbled in the hand, breaking down to pieces of an inch or less in diameter. The freshly broken surfaces were darker in color than the unbroken particles on account of the greater moisture within the agglomerations. The entire mass emitted a pungent acid odor.

The first problem to be considered was the analysis of the "residue". The following table shows the complete composition of the material, and also indicates the desirability of recovering the zinc in the form of the chloride.

H_2O	7.06
Zn	23.05
$ZnCl_2$	15.30
$FeCl_3$	3.72
SiO_2, Al_2O_3, Pb, Cu, C, etc.	50.87
	100.00%

Average percent of total zinc - 30.44%

PROCEDURE.

MECHANICAL CONCENTRATION.

As previously stated, the only suggestipn received from the firm which supplied the material for our work, was to the effect that a jigging scheme be attempted as a possible method of concentrating the zinciferous constituents. In order to obtain a fair sample for such a trial it was necessary to reduce all the material to a minimum size. A small gyratory crusher of the coffee-mill type was used for the preliminary reduction. Difficulties were encountered here on account of the presence of a certain amount of metallics which caused the crusher to choke. This initial crushing gave a maximum size of a half-inch. A screen sample of 500 grams was taken at this point in order to determine the effect of the crushing.

A Rotap machine was employed, yielding thirteen screen products after a thirty minute run. Standard Tyler screens were used, ranging from six to two hundred meshes to the inch. The particles which remained on the largest mesh were flatened metallic pieces not over an inch in length and averaging three-eighths

of an inch in thickness. These particles all showed a metallic fracture, and as was determined later, the zinc content of this screen product was higher than that of any of the other twelve. Analysis of all the screen products proved to be the deciding factor in ruling out the concentration or separation schemes that are based upon specific gravity differences in the metal-bearing and non-metal-bearing constituents of the material under observation. The screen analysis showed that the desired effects of critical crushing could not be obtained, since there was no way to free the metal from the gangue by reducing the size of metal-bearing particles. See table on following page.

The use of the jig, the concentrating table and the flotation plant follow the crushers in the removal of separable metallic components in such instances as permit by virtue of the separation of a profitable percentage of the desired element. The jig and the table were found unsatisfactory since no separation of the zinciferous fraction was noted. It was necessary, of course, to use only the smaller size particles in attempting a separation by use of the jig or the concentrating table. No work was tried

SCREEN ANALYSIS.

Sample 500 grams

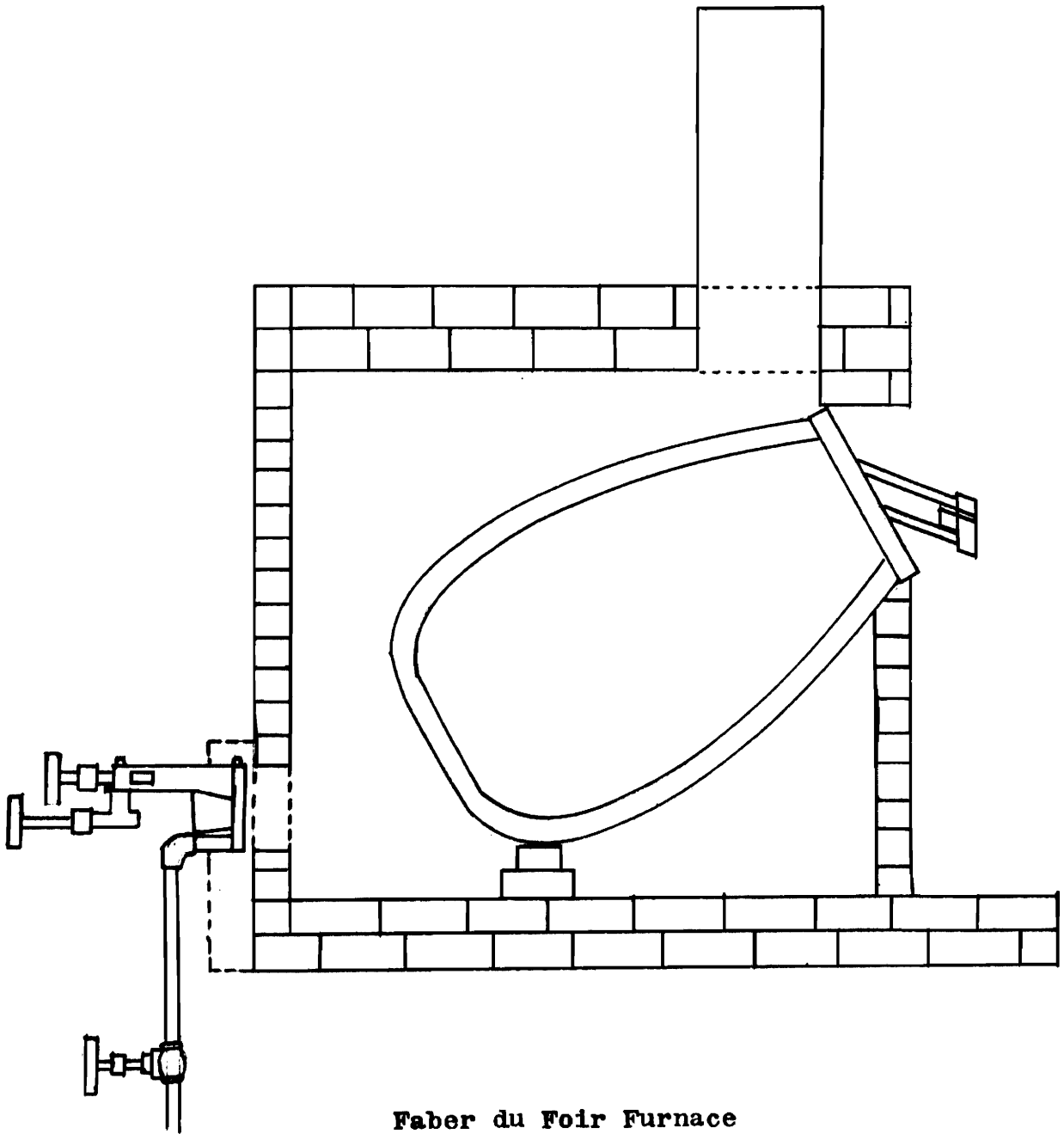
Weight	% of total weight	Screen	Zn content	% total zinc content
33.998	6.7996	on #6	79.52	5.504
45.436	9.0872	thru #6 on #8	20.52	4.996
63.393	12.6787	thru #8 on #10	39.39	4.992
45.337	9.0675	thru #10 on #14	22.13	1.982
36.083	7.2167	thru #14 on # 20	28.61	2.064
49.136	9.8273	thru # 20 on #28	24.14	2.372
44.761	8.9522	thru #28 On #35	22.41	2.006
41.566	8.3132	thru #35 on #48	21.65	1.800
39.956	7.9912	thru #48 on #65	21.88	1.748
34.404	6.8808	thru #65 on # 100	23.36	1.608
26.298	5.2596	thru #100 on #150	28.52	1.500
11.186	2.2373	thru #150 on #200	32.31	.724
28.443	5.6886	thru #200	35.91	2.046
499.997	99.9999			30.196

along the line of flotation because of the apparent difficlty of reducing all the material to the necessary minimum size. The futher disadvantage of excessive crushing costs was also taken into account. Later on there appeared still another argument against a scheme which employed water as a carrier. This objection was due to the solubility of an appreciable portion of the valuable constituent.

SMELTING.

It was next thought that smelting would afford a satisfactory means of recovering the zincky fraction of the material in hand. To this end a Faber du Foir furnace was built. This furnace was built up around a graphite crucible, arranged as in the sketch on the following page. The walls of the crucible were about one inch thick, as was also the lid which was sealed on after the charge had been admitted. The furnace proper was of fire-brick, and it was fired with gas. Several hours were required to reach a temperature of about 1200 degrees centigrade. This temperature was maintained for six hours.

The charge consisted of five pounds of the material. As the temperature rose within the crucible



Faber du Foir Furnace

drops of moisture condensed in the cooler part of the outlet. This moisture was shortly given off in the form of steam as the temperature was gradually raised. The continuous application of heat finally caused the the distillation of the zinc chloride which was part of the charge. This came over as a gray, sirupy liquid which congealed on cooling, and subsequently absorbed considerable moisture from the air.

Following the appearance of the zinc chloride the distillate consisted of metallic zinc. The maximum temperature reached in the crucible did not exceed 1200 degrees,C. This maximum was maintained for six hours,at the expiration of which the quantity of the distillate was so slight as to indicate no further advantage in prolonged heating. The removal of the distillation residue was desirable at this point but there was no convenient means of effecting such removal. Accordingly the crucible was allowed to cool after having been fired for eight hours. The residual mass had sintered, and it was necessary to use a cold chisel to separate the residue from the walls of the crucible.

Examination of the distillation residue demonstrated the undesirability of the smelting procedure, both on account of the low efficiency of the process and the high cost of operation. As is to be seen by consulting the table on the following page, the percent recovery was only half of the total zinc content of the charge. No attempt was made to use an electric furnace in order to secure the more complete extraction due to the higher temperature attainable in such a furnace. The exclusion of all electrical methods was intentional, since the costs incidental to such processes are not compatible with the product to be obtained in this instance.

Previous to this time the use of solvent agents had not been tried on account of the simplicity of the other schemes which were thought to be worthy of trial. The failure of these methods now brought leaching methods into consideration.

DISTILLATION DATA.

Percent zinc in charge, uncombined*	23.05%
Percent zinc in residue, uncombined*	16.81%
Percent zinc in charge as $ZnCl_2$	15.30%
Percent zinc in residue as $ZnCl_2$	none
Percent moisture in charge	7.06%
Percent moisture in residue	none
Percent zinc in charge (total)	30.44%
Percent zinc in charge (total, after being dried at 110° C.)	32.75%

From a consideration of the foregoing it appears that the percent recovery of zinc by the distillation process does not exceed 50% of the non-volatile constituents of the charge.

* Zinc not in the form of the chloride.
*

LEACHING PROCESS.

In connection with a leaching process, one of the first considerations was the selection of an agent which should yield a product requiring little additional handling, if possible. According to previous indications, zinc chloride as the end product ought to be the most easily obtained objective, with the further advantage that such a product supplied a desirable commodity. Hydrochloric acid thus came to be the solvent to be employed.

Thorough digestion of the material to be treated with hydrchloric acid required acid-resistant apparatus. Our needs in this respect were met by several Elyria kettles. The kettles were equipped with covers and stirrers, and they were steam-jacketed. The capacity of these vessels was about one gallon each, and for this reason it was thought advisable to treat such size particles as would bear a ratio to the size of the container somewhat like what might be the case in a commercial operation. This meant the reduction of our material to a certain extent beyond what had already been done.

The reduction of the material was effected by calcining all which would not pass through a No. 2 standard Tyler screen. The heat treatment of the over-size was conducted in iron pots, thus inducing a degree of disintegration of the massive particles. The intensity of the heat was greatest at the bottom of the pots and so caused the accumulation of some metallic zinc there. This "feathered" when the still hot contents of the pots were poured through the cold screen. Since the upper layers of the material were not so intensely heated, there was no loss due to volatilization except for the water vapor which was driven off. The moisture losses were compensated by the additon of calculated amounts of water later on.

After the satisfactory reduction of all the material had been effected, the entire quantity was thoroughly mixed, quartered and coned. In this manner uniform samples of one pound each were obtained. These one-pound charges were used as the basis for the subsequent work on leaching.

In our work on leaching it was thaught to be advisable to note the results of varying the concentrations of the leaching solutions simultaneously with a variation of the temperature. This proved to be impracticable, however, since the changes in temperature could not be controlled as the increases in concentration were gradually effected. Accordingly, a uniform temperature of 100° C. was maintained.

The possibilty of regulating the temperature was within the scope of the work, but the apparent advantage of the higher temperatures was taken as the reason for not constructing a cooling system. The variables were thus reduced to the strengh of the of the solvents and the time for the separate runs.

Beginning with a simple water extraction, the leaching liquor was increased gradually up to six normal hydrochloric. The better results were found to follow the use of an acid solution having a minimum concentration of two normal. The time element varied from an hour and a half to two hours and one half according as the concentration of the acid varied from two to six normal.

The maximum extraction of the water solution was about 7½% and the maximum total extraction was about 30%. In the light of this fact it does not appear advisable to complicate the leaching process by the use of varying solutions. A series of tanks allowing the passage of concentrated hydrochloric acid to the point of saturation, followed by a wash of plain water therefore solves the problem.

The ratio of solution to solids was 1200 cc. to one pound. This ratio was kept constant in all the tests after various different ratios had been tried and had been found less satisfactory than the one we ultimately adopted.

CONCLUSIONS

The system most readily devised for extracting zinc from the material of these experiments has been indicated in the foregoing pages. The use of hydrochloric acid as a medium of producing a salable commodity, zinc chloride, affords an economical means of salvaging this waste material.

In the use of such a solvent there results incidentally the formation of a sludge. This sludge can be handled in a centrifuge or by an Oliver filter if desired. The washings coming from the tanks proper may be collected in evaporating vats if a dry product is required. The original solutions are not to be drawn off until they have reached a specific gravity of 1.40, approximately, as this is the gravity of a concentrated solution of zinc chloride.

The final product produced in the above manner has a slight percentage of impurities, but the use of the zinc chloride for commercial purposes is not hampered by the presence of those impurities. Should there be any particular need for a purer product the usual process of recrystallization offers a remedy.

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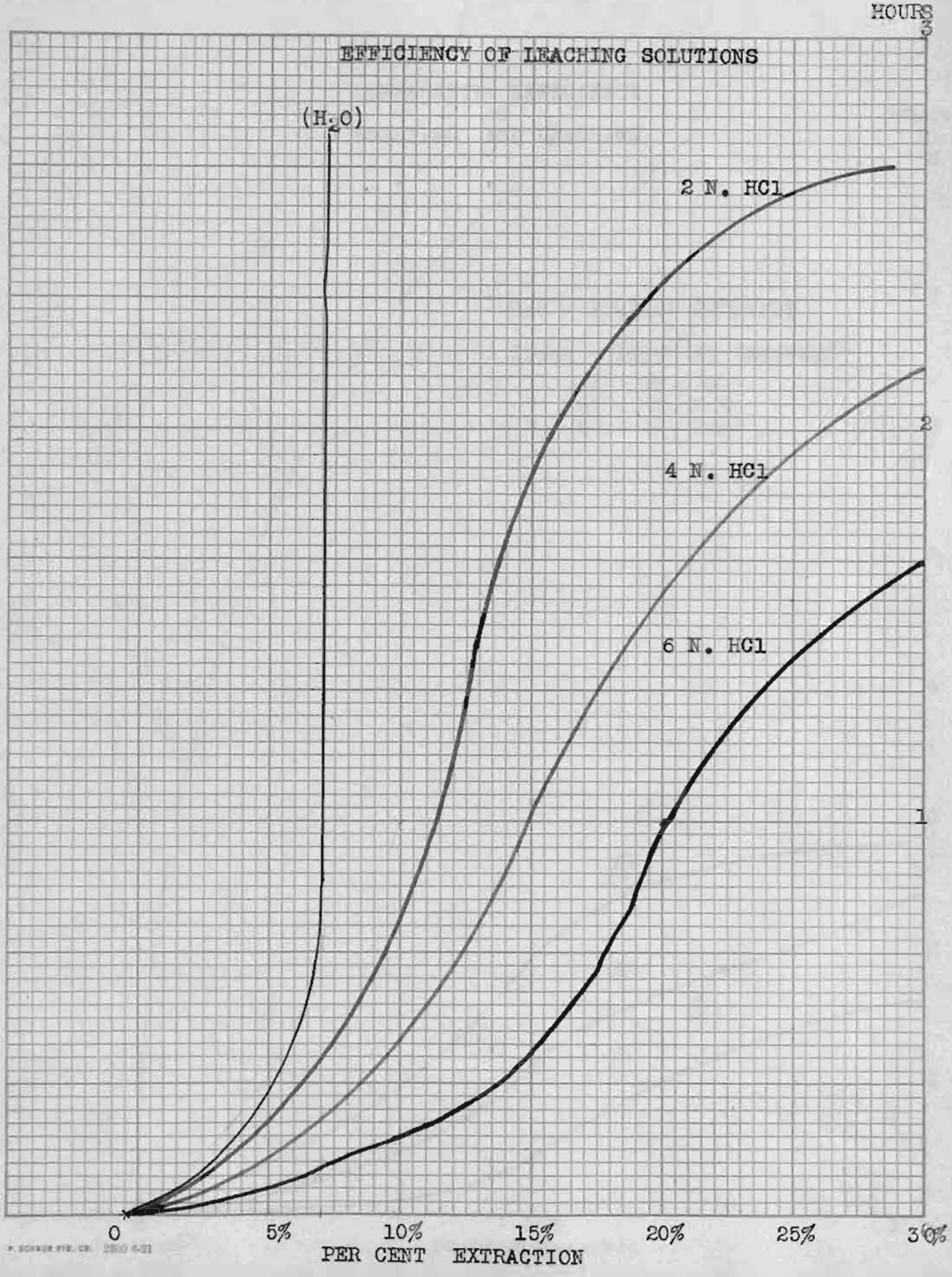

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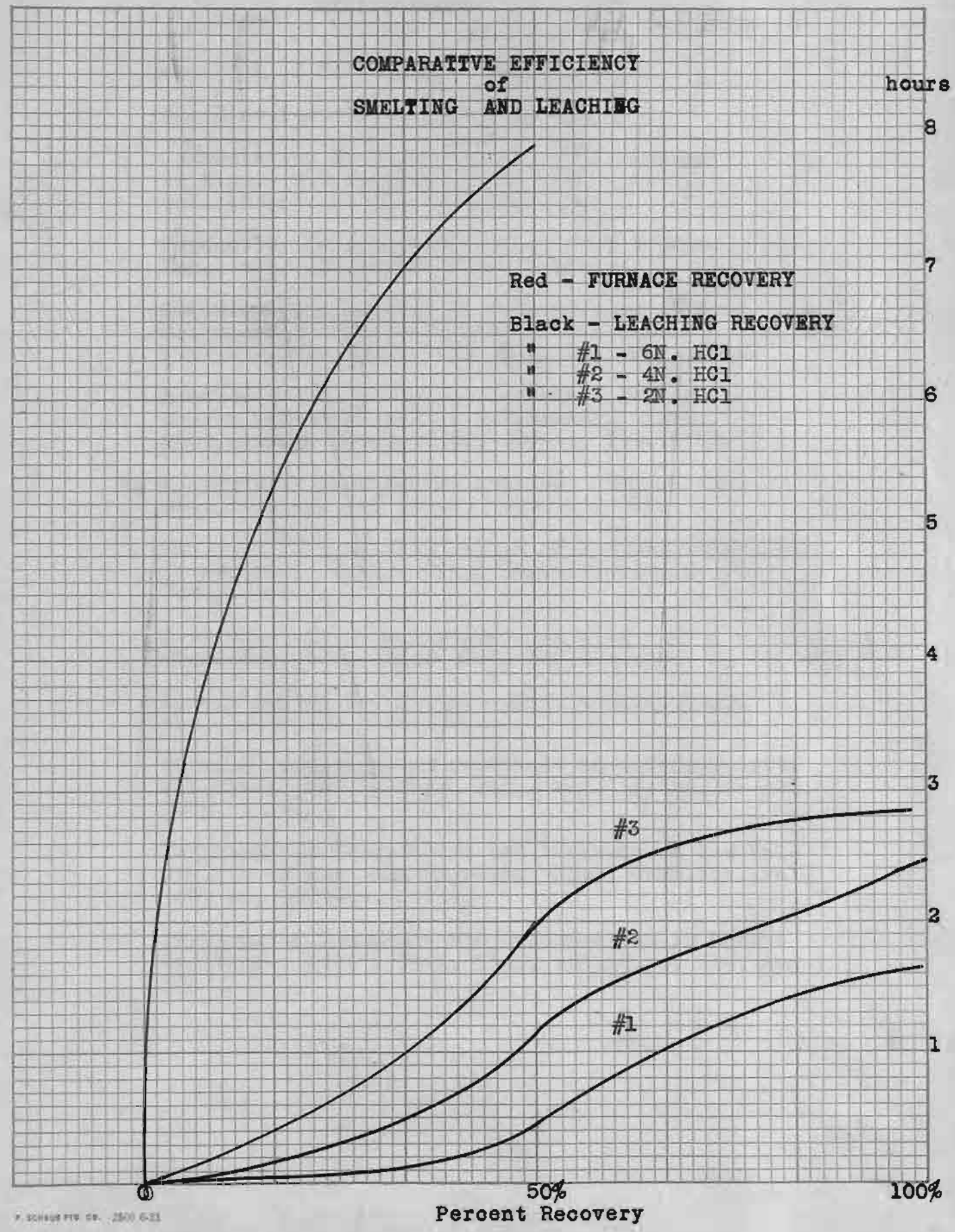

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